The mechanism of dissolution of minerals in acidic and alkaline solutions: Part I — A new theory of non-oxidation dissolution

F.K. Crundwell

CM Solutions (Pty) Ltd, Building T5 Pinelands, 1 Ardeer Road, Modderfontein 1609, South Africa

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ABSTRACT

A new theory for the description of the kinetics of non-oxidative dissolution reactions is proposed. The theory accounts for the breaking of bonds between the constituents of a solid, which results in charged species, and the simultaneous transfer of these charged species across the potential difference that exists at the surface. When the minerals under consideration dissolve, anions and cations are formed in the solution. The model focuses on the formation of these anions and cations. The processes leading to the formation of anions are considered to be independent of those leading to the formation of cations. However, they are coupled by the potential difference across the Helmholtz layer, since the rate of formation of both anions and cations is dependent on this potential difference. The model predicts orders of reaction that are either 0.25, 0.5, 1.0 or 1.5 with respect to H^+ or OH^- ions in the solution. The predictions of the theory for various reaction scenarios are presented. The model is consistent with the experimental data reported in the literature for a wide range of minerals dissolving in acidic or alkaline solutions.

1. Introduction

The dissolution of minerals by acids is important in the fields of geochemistry, materials science and hydrometallurgy. Knowledge of the mechanisms of dissolution is a primary goal of these fields. Such knowledge can aid in the design of operations where dissolution or etching is required and can be used to predict the behaviour of minerals in solutions.

In hydrometallurgy, the dissolution (or leaching) of the mineral is a prerequisite step to the production of valuable metal products. The production of copper, nickel, zinc, gold, manganese and other metals requires a leaching step prior to purification in aqueous solutions, and the winning of the metal as a saleable product.

Knowledge of the kinetics and mechanisms of dissolution is fundamental to an understanding of many of the reactions important in geochemistry. The dissolution of silicates and carbonates affects the chemistry of soils, water aquifers, oil reserves, and schemes for the sequestration of carbon dioxide.

Dissolution reactions can be divided into two classes: those that involve a change in valence state, and those that do not (Crundwell, 2013). The reactions of the first class are referred to as oxidative reactions if the mineral is oxidized, and reductive if it is reduced. The reactions of the second class, in which the mineral is neither oxidized nor reduced, are referred to as non-oxidative reactions. It is the kinetic mechanism of this class of non-oxidative dissolution reactions that is the subject of this paper.

Three examples of non-oxidative dissolution reactions that are typical are the dissolution of copper oxide:

$$CuO + 2H^+ \rightarrow Cu^{2+} + 2H_2O \tag{1}$$

the dissolution of sphalerite:

$$ZnS + 2H^+ \rightarrow Zn^{2+} + H_2S \tag{2}$$

and the dissolution of calcium carbonate:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \tag{3}$$

The simplicity of these non-oxidizing reactions is their own justification for study. If these reactions can be shown to conform to a generalized framework, our scientific understanding improves dramatically. The purpose of this paper is to propose such a generalised theory of the dissolution of minerals in non-oxidizing solutions. Subsequent papers demonstrate how classes of minerals conform to this theory. In particular, the behaviour of silicate minerals is examined in Part II, and the behaviour of oxides and sulphides is examined in Part III of this series of papers.

The paper is structured in the following manner: The importance of the order of reaction as the key kinetic parameter is emphasised in the next section. A review of the reported orders of reaction is then presented, followed by a review of the models of dissolution kinetics in current use.

E-mail address: frank.crundwell@cm-solutions.co.za.

It is argued that these models do not successfully describe the orders of reaction, and as such, they need to be reassessed. The development of the new mechanism proposed in this paper starts with a description of the mineral–solution interface, followed by the derivation of the proposed theory of dissolution that describes the experimentally determined orders of reaction.

2. The kinetic parameters: order of reaction and activation energy

Any proposal for a mechanism of reaction must be able to describe the measured rates of reaction. The rates of dissolution reactions are influenced by the temperature, and by the concentrations of reagents in solution. This dependence is frequently expressed in the following relationship for an irreversible reaction:

$$rate = k[c]^n \exp(-E_A/RT) \tag{4}$$

where k represents the rate constant, $[c]$ the activity or concentration of a reagent in solution (either dimensionless or mol/m^3), n the order of reaction, E_A the activation energy (J/mol), R the gas constant (J/mol/K) and T the temperature (K).

The two parameters in the rate expression are the order of reaction, n, and the activation energy, E_A. The activation energy indicates how strongly dependent the rate of reaction is on temperature. The higher the activation energy, the more the rate is affected by temperature.

The activation energy for dissolution reactions is generally found to be less than 20 kJ/mol if the rate is controlled by diffusion in the solution, and greater than 40 kJ/mol if the rate is controlled by chemical reaction (Burkin, 1966).

The order of reaction describes the type of dependence that the rate of reaction has on the concentration of a reagent in solution. For example, if the value of n is one, then the rate of reaction is said to be first order. If it has a value of two, it is said to be second order. The order of reaction is important in interpreting the mechanism of reaction; a proposed mechanism of reaction does not gain acceptance if it does not predict orders of reaction whose values are similar to those determined experimentally.

Table 1
Kinetic parameters for a variety of non-oxidative dissolution reactions.

Mineral formula	Solution	Reaction order wrt H$^+$	Activation energy, kJ/mol	Reference
BeO	HCl	0.49		Vermilyea (1966)
	H$_2$SO$_4$	0.49		Vermilyea (1966)
	H$_2$C$_2$O$_4$	0.57		Vermilyea (1966)
MgO	HNO$_3$	0.49	57	Jones et al. (1978), Terry (1983)
Mg(OH)$_2$	HCl	0.47		Vermilyea (1969)
MgSiO$_4$	H$_2$SO$_4$	0.36	67	Sanemasa et al. (1972), Terry (1983)
	HCl	0.42	59	Sanemasa et al. (1972), Terry (1983)
	HClO$_4$	0.40	59	Sanemasa et al. (1972), Terry (1983)
ZnO	HCl	0.55	41	Danilov et al. (1976), Ramachandra Sarma et al. (1976), Terry and Monhemius (1983)
	HClO$_4$	0.67	41	Terry and Monhemius (1983), Terry (1983)
ZnSiO$_4$	HCl	0.45	45	Terry and Monhemius (1983), Terry (1983)
	HClO$_4$	0.4	45	Terry and Monhemius (1983), Terry (1983)
	HNO$_3$	0.38	45	Terry and Monhemius (1983), Terry (1983)
	H$_2$SO$_4$	0.5	49	Terry and Monhemius (1983), Terry (1983)
ZnFe$_2$O$_4$	H$_2$SO$_4$	0.6	63	Ramachandra Sarma et al. (1976), Terry (1983)

Since the order of reaction is the prime parameter for any discussion of the mechanism of dissolution, it is worth briefly reviewing the experimentally determined values. These orders of reaction are reviewed in the next section.

3. Typical values for experimentally-determined orders of reaction for non-oxidative dissolution

The rate of dissolution of minerals in non-oxidizing solutions is mainly dependent on two types of constituents of the solution. Firstly, the rate is dependent on the pH, which indicates that the H$^+$ ion (or alternatively the OH$^-$ ion) is primarily responsible for dissolution. Secondly, the rate is dependent on the concentration of anions (or ligands) that might form complexes with the metal ion.

When the orders of reaction with respect to H$^+$ are compared, a somewhat surprising result emerges. The orders of reaction are close to either one half or one. For example, Majima et al. (1981) reported that the rate of dissolution of CuO, given in Eq. (1), is half order in H$^+$ in solutions of sulphuric acid, and first order in solutions of perchloric, hydrochloric and nitric acids.

This pattern of either first order or half order, which is particularly interesting, occurs for a diverse range of minerals. For example, Terry (1983) studied the rates of dissolution for a several silicate minerals and compiled a list of the orders of reaction with respect to H$^+$. The results for the series of minerals shown in Table 1 indicate that the value of the order of reaction is close to one half.

Another interesting feature of these types of reactions is the values of order of reaction for the reverse reaction. Crundwell and Verbaan (1987) studied both the forward and reverse reactions for the dissolution of sphalerite (ZnS). They reported that even though the order of the forward reaction was first order with respect to H$^+$, the order of the reverse reaction was one-half order with respect to H$_2$S and Zn^{2+}. Locker and de Bruyn (1969) reported similar results for CdS. This means that the analysis of the reverse reaction is perhaps as important as that of the forward reaction in understanding leaching and dissolution reactions.

The specific purpose of this work is to provide a unifying framework that describes the orders of reaction, and hence is able to describe the mechanism of non-oxidative dissolution. Prior to doing that, a brief discussion of the models in current use is reviewed.

4. Review of the models of dissolution of minerals in non-oxidizing solutions

There are four models that are currently used to interpret the rate of dissolution reactions (i) the adsorption model, (ii) the surface complexation model, (iii) the precursor-species model, and (iv) the ion-transfer model. Each of these models will be discussed in turn.

4.1. Adsorption model

This model envisages that the rate of dissolution is dependent on adsorbed species on the surface. Consider the reaction of H$^+$ in the solution with a site on the surface, given as follows:

$$\circ \quad + \quad H^+ = \quad \bullet H^+ \tag{5}$$

where $\circ$ represents an available or unoccupied site, and $\bullet H^+$ represents an occupied site. The proportion of the total surface that is occupied by $\bullet H^+$ is given by θ. The net rate of the adsorption onto the surface, r_{ads}, is given by:

$$r_{ads} = k_1 \left[H^+ \right] (1-\theta) - k_{-1}\theta \tag{6}$$

where k_1 is the rate constant for the forward (adsorption) reaction (m/s) and k_{-1} is the rate constant for the reverse (desorption) reaction (mol/m²/s). The units of r_{ads} are mol/m²/s, and θ is unitless.

If it is assumed that the adsorption and desorption of H^+ are faster than other surface phenomena, such as dissolution, then this rate is close to zero by the pseudo-steady state assumption, and an expression for θ can be derived:

$$\theta = \frac{k_1[H^+]}{k_{-1} + k_1[H^+]}. \tag{7}$$

Expressions of this form describe the coverage of the surface in terms of a monolayer of adsorbent, and are referred to as Langmuir isotherms.

The adsorption model of dissolution postulates that rate of dissolution is proportional to the concentration of occupied sites on the surface. In this case, the rate of dissolution is given by:

$$rate = k\theta. \tag{8}$$

The substitution of Eq. (7) into Eq. (8) yields the following overall expression for the rate of dissolution according to the adsorption model:

$$rate = \frac{kk_1[H^+]}{k_{-1} + k_1[H^+]}. \tag{9}$$

The adsorption model envisages that the rate of dissolution is affected by the adsorption of H^+ onto the surface. At low concentrations of $[H^+]$, the term $k_1[H^+]$ is less than the term k_{-1}, so that the rate of dissolution is first order.

As the concentration of H^+ increases, the term $k_1[H^+]$ becomes much greater than the term k_{-1}. When this occurs, the rate of dissolution becomes zero order in H^+ and the rate is no longer affected by further increases in the concentration of H^+. At this point, the rate has reached a maximum value, sometimes referred to as saturation.

Interestingly, this simple model is not supported by the experimental results. The experimental orders of reaction are either half order or first order, and there is no suggestion of saturation. In addition, it only applies at conditions far from equilibrium. An alternative form of adsorption is the surface-complexation model. This model has been adapted to describe dissolution, and is considered next.

4.2. Surface-complexation model

The surface-complexation model is based on the concept that the ions at the surface of the mineral bond and form complexes with species in the solution (Hayes and Katz, 1996). These complexes at the surface then depart, resulting in dissolution. Thus, the advocates of this model claim that it is not the concentration of the chemicals in solution that drives dissolution; rather, it is the concentration of the complexes on the surface that is the driving force.

This postulate can be expressed as a rate law in the following form:

$$rate = k[>M-L]^p \tag{10}$$

where k is a rate constant, and p is an order of reaction with respect to the concentration of a species on the surface that controls the rate of reaction.

As mentioned, this model envisages the formation of a chemical species on the surface that controls the rate of reaction. The chemical species that is frequently responsible is H^+, so ">$M - L$" might in this case represent a protonated site on the surface of the dissolving mineral, and this form of the model is called the 'proton-promoted surface complexation model'.

The concentration of ">$M - L$" is measured by titration since it is assumed that the formation of ">$M - L$" is much faster than the rate of dissolution. For dissolution by acid, the concentration of the protonated surface and the rate of dissolution have been determined, making it possible to obtain values for p. For example, Furrer and Stumm (1988) determined that the value of p for BeO is 2 and p for Al_2O_3 is 3. Zinder et al. (1988) argued that the value of p for α-FeOOH is 3.

Several criticisms of this model have been raised: (i) It is difficult to discern a systematic pattern in the value for p (Brady and House, 1996). This is very surprising in the light of the values shown in Table 1, which demonstrate a fascinating similarity in the order of reaction when expressed in terms of the concentration in solution. (ii) It is difficult to interpret or associate a meaning with the parameter p. In general kinetics, this would be a reaction order, but in this case, the model surely cannot be suggesting that three surface complexes react together, which is what a value of p equal to 3 suggests. Suggestions have been made that the value of p is equal to the valence of the metal ion in the solid; however, this suggestion is not general (Casey and Ludwig, 1996). Without any clear interpretation of model parameters, the model is robbed of its meaning. (iii) In order to obtain values for the order of reaction with respect to H^+ that are fractional, the proponents of the model simply assume that the rate of reaction is one-half order. In other words, there is no explanation, derivation or interpretation of the order of reaction with respect to H^+. (iv) The model can only describe dissolution reactions far from equilibrium. A thorough model of dissolution of non-oxidizing reactions should be able to incorporate the equilibrium conditions.

4.3. Precursor species model

The precursor species model that has been developed by Oelkers (2001) is a form of the surface complexation model. This model differs from the surface-complexation model in that it proposes the existence of a precursor species. This precursor species, which is bound to the surface, is assumed to be in equilibrium with both the reactants and the surface. The precursor species is also in equilibrium with an activated complex, and this activated complex breaks down to form the reaction products. Conceptually, this model can be expressed as follows:

$$surface + aqueous\ species \Longleftrightarrow precursor \Longleftrightarrow activated\ complex \rightarrow products. \tag{11}$$
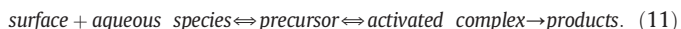
This model does not predict orders of reaction with values close to one half with respect to H^+ ions in the solution. Instead, at a critical juncture in the derivation, it is simply assumed that a surface species is in equilibrium with half a proton, and this gives rise to the half-order kinetics. This is simply solving the problem of fractional orders by making the stoichiometry fractional (see Eqs. (2a) and (2b) in Pokrovsky and Schott, 2000; and 24 and 25 of Schott et al., 2009). This is an error, an incorrect application of the methods of chemical kinetics. Half a proton cannot be a participate reactant in an elementary step. Consequently, the precursor model is incorrectly formulated. Because the precursor model is not a properly constructed kinetic model consisting of elementary reactions, the only conclusion that can be drawn is that the precursor model has not correctly identified the mechanism of dissolution.

4.4. Ion-transfer mechanism

Vermilyea (1966) proposed that the dissolution of ionic solids was dependent on the transfer of ions from the surface to the solution (see also Engell, 1956; Diggle, 1973). The rate of transfer of ions is exponentially dependent on the potential difference between the solid and solution. Vermilyea proposed that the rate of transfer of cations is equal to the rate of removal of anions, so that charge neutrality is maintained in both bulk phases. Since the potential difference has an opposite effect on the rate of transfer of anions and cations, the charge neutrality condition provides a relationship to solve for the potential difference and to derive a rate expression that is only dependent on observable kinetic factors, that is, concentration and temperature.

The rate expression derived by Vermilyea (1966) is given as follows:

$$rate = \left(k_+ n_+\right)^{1-\zeta} \left(k_- n_- \left[H^+\right]\right)^{\zeta} \tag{12}$$

where k represents a rate constant with respect to individual ions, n is the surface concentration of ions of the ionic solid, $[H^+]$ is the concentration of H^+ in solution. The subscripts '+' and '−' represent cation and anion of the ionic solid, respectively.

The order of reaction with respect to H^+ is ζ which is given by $\alpha_+ z_+/(\alpha_+ z_+ - \alpha_- z_-)$, where α are charge-transfer coefficients for the transfer of ionic charge from the surface to the outer Helmholtz plane, and z is the charge of the dissolving anion or cation (Crundwell and Verbaan, 1987). The value of α_+ is expected to be close to α_-, and if the charges of the ions are equal, then the value of ζ is 0.5. Therefore, the ion-transfer mechanism of Vermilyea predicts values for the order of reaction that are close to the experimental results shown in Table 1.

However, the model is limited to ionic solids, and it accounts only for the transfer of ionic charge from the surface of the solid across the Helmholtz layer. This model has gained limited acceptance for the dissolution of metal oxides, but it has not gained purchase in the study of minerals like the silicates. A major aim of this work is to be able to describe the dissolution of minerals. For example, consider the dissolution of brucite, $Mg(OH)_2$. The value given in Table 1 for the order of reaction of $Mg(OH)_2$ with respect to H^+ is 0.47. The ion-transfer mechanism predicts an order of reaction with a value of $0.5(2)/(0.5(2) - 0.2(-1))$, which is equal to 0.66. This prediction is much better than the surface-complexation and precursor models, which simply assume fractional orders of reaction without a mechanistic derivation. However, as pointed out by Vermilyea (1969), the value calculated by the ion-transfer model still seems quite distant from the experimental values.

In the next section we briefly review the requirements for a comprehensive theory of dissolution.

5. Requirements for a theory of dissolution in non-oxidizing solutions

A comprehensive mechanism of dissolution needs to address at least two aspects of dissolution:

(i) the mechanism must describe the changes in rate of dissolution as a function of the composition of the solution — in particular, it must describe the observed orders of reaction; and,

(ii) the mechanism must be able to account for changes in the rate of dissolution of minerals as a function changes in composition of the solid — for example, the series of orthosilicate minerals Mg_2SiO_4, Zn_2SiO_4, Mn_2SiO_4, etc., or the effect of substitution in solid solutions (Casey, 1991).

The focus of this paper is on developing a theoretical framework that is able to account for the first of these requirements. The mechanism of dissolution that is proposed in this paper is based on the breaking of bonds at the dissolving surface and the transfer of charge across the interface. The mechanism includes both forward and reverse reactions. The theory is then applied in Parts II and III to demonstrate how it can be applied to the dissolution of silicates, sulphides and oxides.

6. The mechanism of dissolution in acidic solutions and alkaline solutions

Mineral solids are composed of atoms that are bonded by covalent and ionic bonds. As the solid dissolves, these atoms become less bonded to one another and form more energetically favourable bonds with components in the aqueous phase. In the atoms of the solid becoming less bonded to each other, the bonds break, and the atoms of the solid become charged as they depart from the surface of the solid.

The interface between the bulk of the solid and the bulk of solution is invariably charged, due mainly to two factors (i) the termination of the solid structure leaving unsaturated bonds (referred to as Tamm and Shockley states) and (ii) the adsorption of charged species present in the solution onto the surface. Although Shockley states have a low concentration (10^{12} cm^{-2}), they can significantly influence the electronic processes at the interface (Memming, 2001). The source of the potential difference across the surface of an inert solid is mainly a result of adsorption (Miller et al., 1995). These features lead to three regions of changes in potential, as shown in Fig. 1. The first region is the potential difference that occurs between the bulk of the solid and the surface of the solid, and is referred to as the space-charge layer, $\Delta^{b-s}\phi$. The second region is between the surface and the 'outer Helmholtz plane', $\Delta^{s-ohp}\phi$, which is the distance of closest approach of non-adsorbed ions (Bockris and Reddy, 1970; Morrison, 1980). This second region is referred to as the Helmholtz layer. The third region, called the Gouy–Chapman layer, $\Delta^{ohp-gc}\phi$, occurs between the outer Helmholtz plane and the bulk of the solution. The potential difference across the Gouy layer is expected to be small because most dissolution is conducted in solutions in which the concentration of the background electrolyte is relatively high.

The electric field, which is the change in potential as a function of distance, is by far the greatest across the Helmholtz layer. During dissolution bonds break to form ions, and these ions must move to the solution under the accelerating or retarding influence of this field. Since the field is highest in exactly the region that is critical to dissolution, the focus of the model will be on the Helmholtz layer. It is the accounting for this charged interface that allows us to correctly account for the orders of reaction reported for the dissolution of various minerals.

In the next section, the rate of bond breaking at the surface is discussed. This background information is then used to derive a model for the rate of dissolution in acidic and alkaline solutions.

6.1. Removal of a species from the surface

A charge-formation and transfer reaction is that in which a species at the surface of a solid breaks its bond with the lattice, forms an ion, and moves as an ion into solution (under the influence of a potential difference between the two phases). This reaction mechanism is shown in Fig. 2.

The reaction shown in Fig. 2 may be represented as follows:

$$\triangleright M_{lat} + wH_2O = M^{z+}(aq) + \triangleright^{z-} \tag{13}$$

where $\triangleright M_{lat}$ represents a species in a lattice position on the surface, $\triangleright^{z-}$ represents the uptake of the excess charge that results from bonds breaking by the surface of the solid, and w represents the stoichiometric coefficient with respect to water.

The symbol $\triangleright^{z-}$ can also be interpreted as an electron, a hole or a charged species at the surface that forms as a result of bond breaking. The electron or hole may not necessarily be mobile — it may be captured by surface states and dangling bonds at the surface and contribute to the potential difference. The significance of this is that the proposed model is not limited to solids that are either conductors or ionic solids; it applies equally to solids that are conductors, insulators and ionic solids.

The bond between the species and the solid diminishes with increasing distance from the surface. At the same time, the interaction with the solvent becomes stronger. This breaking and formation of bonds, and its associated movement of charge have an activation barrier that depends on the distance from the surface, as shown in Fig. 3.

The highest point of the activation barrier usually occurs close to midpoint between the surface and the outer Helmholtz layer. Like other chemical reactions, the height of the activation barrier is dependent on temperature. Unlike other reactions, the height of the activation barrier is also influenced by the electric field in the Helmholtz layer, which is illustrated in Fig. 4. A direct consequence of the influence on
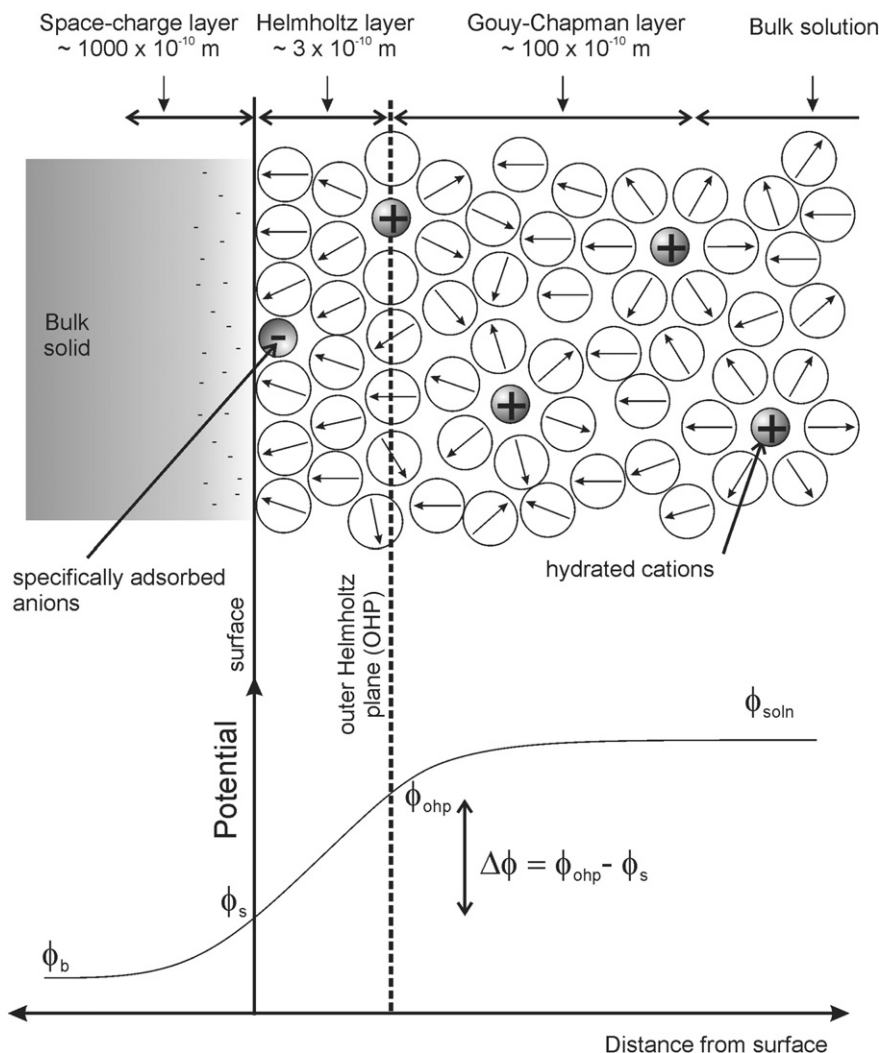
Fig. 1. The structure of the charge interface, showing the changes in potential due to the space-charge layer, the Helmholtz layer and the Gouy–Chapman layer. In the mechanism proposed here, it is the *change* in potential difference over the *Helmholtz layer* that influences the kinetics of reaction. The symbol ϕ refers to the electrical potential, and the subscripts *b*, *s*, *ohp*, and *soln* refer to bulk solid, surface, outer Helmholtz plane, and bulk solution, respectively.

the electric field (or potential difference) on the activation energy is that there is an exponential relationship between the rate of reaction and the potential difference between the surface and the outer Helmholtz plane.

The rate of the reaction given in Eq. (13), *r*, is a function of potential difference, $\Delta\phi$, between the surface and the outer Helmholtz plane (Bockris and Reddy, 1970; Butler, 1924, 1932; Erdey-Grusz and Volmer, 1930; Vetter, 1967):

$$r = k_a[M_{lat}][H_2O]^w \exp(\alpha F\Delta\phi/RT) - k_c\left[M^{z+}\right] \exp\{-(1-\alpha)F\Delta\phi/RT\} \quad (14)$$

where $[M_{lat}]$ and $[M^{z+}]$ refer to the surface and solution concentrations (or activities) of M_{lat} and M^{z+}, respectively, $[H_2O]$ is the activity of water, α is the transfer coefficient, and k_a and k_c are the rate constants for the forward (dissolution) and reverse (deposition) reactions, respectively.

The use of Eq. (14) does not necessarily imply that the rate limiting step is electron transfer. Indeed even in electrochemical reactions, the rate is not determined by electron transfer as such, but by the reorganization of the solvation sheath around the ion. Dissolution in this context involves the removal of the species M (or A) from the surface and the formation or rearrangement of the solvation sheath around the departing ion by hydration. The use of Eq. (14) implies that these bond-breaking and solvation processes are dependent on changes of

the interfacial potential difference. (See Appendix A for a brief discussion of Eq. (14) in the context of this paper.)

The potential difference, $\Delta\phi$, between the surface and the outer Helmholtz plane is equal to $\phi^s - \phi^{ohp}$ as shown in Fig. 1, and was referred to earlier as $\Delta\phi^{s - ohp}$. The value of α is expected to be close to one-half because the saddle point of the activation barrier occurs approximately midway between the surface and the outer Helmholtz layer, as illustrated in Fig. 3.

This description of the rate of transfer of charged species across the Helmholtz layer is used to derive a rate expression for dissolution in the sections that follow.

6.2. Description of the dissolution phenomena

The steps involved in the dissolution of the mineral MA are shown in Fig. 5. In its simplest form, the mechanism occurs in two parallel steps. In the first step, the M species at the surface reacts with *w* water molecules and are removed from the surface and transferred to the outer Helmholtz plane, as described earlier and illustrated in Fig. 2. The removal of M species from the surface is shown as step (a) in Fig. 5.

In the second step, the A species at the surface react with *t* H$^+$ ions at the Helmholtz plane. As the bond between the surface and the A species stretches and becomes weaker, the bonding with the H$^+$ ion increases, resulting in the formation of an activated complex. If there is sufficient
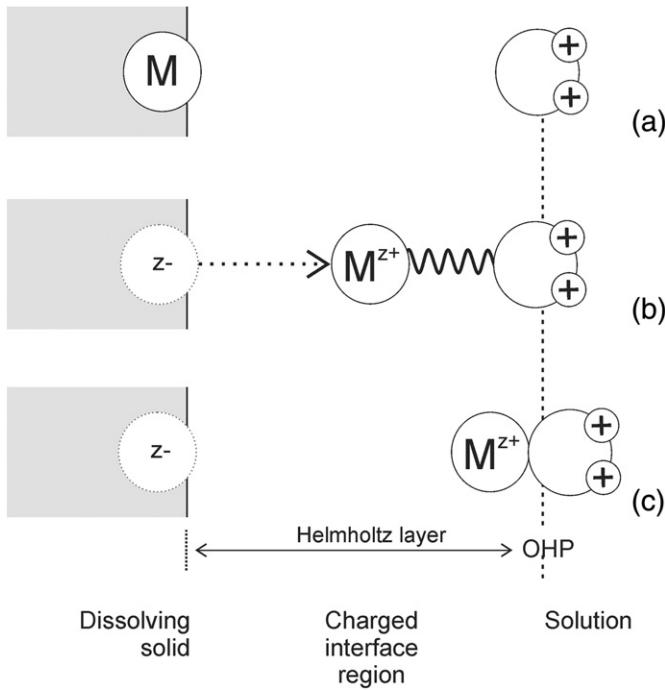
Fig. 2. The movement of a species of the solid from a position at the surface to a position at the outer Helmholtz plane: (a) surface species before reaction; (b) the breaking bond with the surface, represented by the dotted arrow, and the formation of the bond with water; (c) the metal ion at the outer Helmholtz plane.

energy, the activated complex reacts to form the reaction product, in this case H_tA^{t-a}. In other words, the bond with the surface breaks and the bond with H^+ in solution forms, resulting in the formation of an anion and the transfer of the anion to the solution as H_tA^{t-a}.

These two steps, the formation of the cation and the anion, are independent and parallel phenomena. They are also coupled in the sense that they are both exponentially dependent on the potential difference across the Helmholtz layer, $\Delta\phi$. The removal of A and M species from the surface will alter the potential difference across the Helmholtz layer. For congruent, stoichiometric dissolution to be maintained, the rate of removal of A species must be equal to that of M species. The potential of this 'freely-dissolving' surface is determined by the rate of removal of both M and A from the surface. (Some arguments against the model of Vermilyea (1966) have been raised that may be construed as being applicable to the mechanism proposed here. These arguments are addressed in Appendix B.)

6.3. Derivation of the rate of dissolution in acidic solutions

A rate equation for the dissolution of a mineral in acidic solutions at conditions that are far from equilibrium will be developed first. This rate expression will then be expanded to account for (i) the reverse reaction so that it is applicable to conditions close to equilibrium, (ii) specific adsorption, (iii) complex formation, and (iv) dissolution in alkaline solutions.

6.3.1. The rate of dissolution far from equilibrium
The rate of dissolution far from equilibrium is considered in this section. Experiments far from equilibrium are used extensively to establish the correct orders of reaction without the complication of reverse reactions.

The removal of cations from the surface is represented as the following reaction:

$$\triangleright M_{lat} + wH_2O \rightarrow M^{z+}(aq) + \triangleright^{z-} \tag{15}$$

The rate of removal of these cations is described by the following equation:

$$r_+ = k_{a,+}[M_{lat}][H_2O]^w \exp(\alpha_+F\Delta\phi/RT) \tag{16}$$

where the subscript '+' refers to the removal that leads to the formation of a cation. Note that the order of reactions for the reactants reflects the stoichiometry in Eq. (15), so that this rate expression is a properly formulated as an elementary reaction.

The removal of anions from the surface may occur by reaction with protons in the solution (that is, at the outer Helmholtz plane). This reaction is represented as follows:

$$\triangleright A_{lat} + tH^+ \rightarrow H_tA^{t-a} + \triangleright^{a+} \tag{17}$$

where t is the stoichiometric number of protons in this reaction and a is the charge of the (unprotonated) anion.

The rate of this reaction is given by:

$$r_- = k_{a,-}[A_{lat}]\left[H^+\right]^t \exp(-\alpha_-F\Delta\phi/RT) \tag{18}$$

where the subscript '−' refers to the removal that leads to the formation of an anion. $[H^+]$ represents the concentration or activity of H^+ at the outer Helmholtz plane, which is the same as that in the bulk solution. Note that the order of reactions for the reactants reflects the stoichiometry in Eq. (17), so that these reactions are properly formulated elementary reactions.

The rate removal of anions, r_-, is equal to the rate of removal of cations, r_+ by stoichiometry of the overall reaction. This condition yields the following expression:

$$k_{a,-}[A_{lat}]\left[H^+\right]^t \exp(-\alpha_-F\Delta\phi/RT) = k_{a,+}[M_{lat}][H_2O]^w \exp(\alpha_+F\Delta\phi/RT). \tag{19}$$
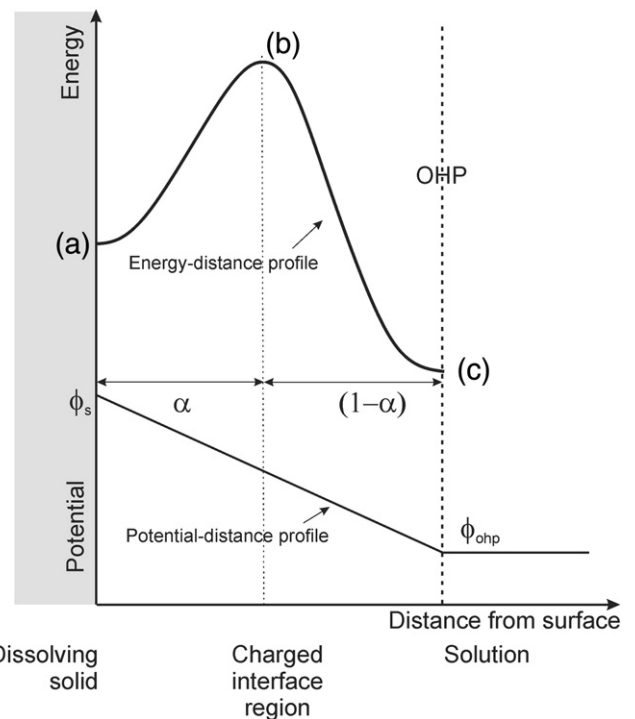
Fig. 3. The activation barrier for the removal of a metal species from the surface and the potential-distance relationship across the Helmholtz layer. Because the reaction is constrained between the surface and the outer Helmholtz plane, the activation barrier occurs within the Helmholtz layer, and the peak frequently coincides with the mid-point of the Helmholtz layer.
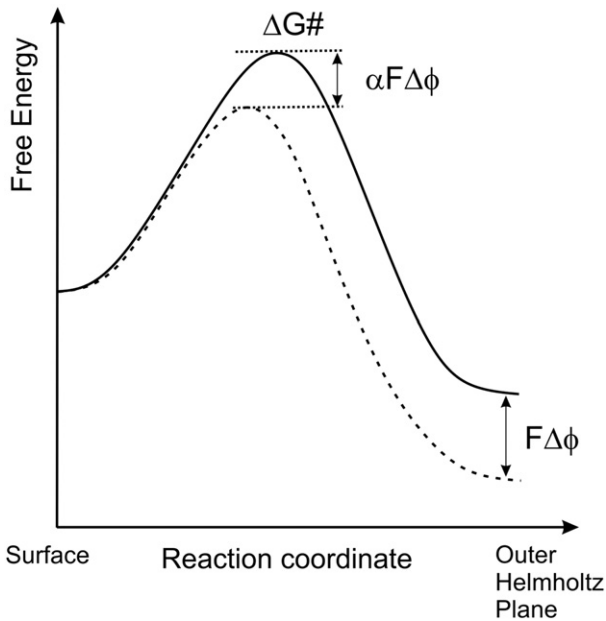
Fig. 4. The effect of electrical potential on the height of the activation barrier. The dotted line represents the effect of a positive change in potential on the free energy along the reaction coordinate. The effect of this is to lower the barrier for the oxidation reaction, so that the forward reaction is favoured.

Eq. (19) can be rearranged to give an expression for the potential difference across the Helmholtz layer of the dissolving surface. This expression is given as follows:

$$\Delta\phi = \frac{RT}{F(\alpha_+ + \alpha_-)} \ln\left(\frac{k_{a,-}[A_{lat}][H^+]^t}{k_{a,+}[M_{lat}][H_2O]^w}\right). \tag{20}$$

The forward rate of the reaction far from equilibrium, $\overrightarrow{r}$, is obtained by substituting Eq. (20) back into Eq. (16):

$$\overrightarrow{r} = \left(k_{a,+}[M_{lat}][H_2O]^w\right)^{1-\overline{x}} \left(k_{a,-}[A_{lat}]\right)^{\overline{x}} [H^+]^{\overline{x}t} \tag{21}$$

where $\overline{x} = \alpha_+/(\alpha_+ + \alpha_-)$. All the constant terms can be lumped together to give the following expression:

$$\overrightarrow{r} = \overrightarrow{k}[H^+]^{\overline{x}t}. \tag{22}$$

The order of reaction is given by xt. It can be calculated for several scenarios. Consider for example the situation where the charge transfer coefficients are either approximately equal to each other so that $\alpha_+ \approx \alpha_-$. This means that the value of $\overline{x}$ in Eq. (20) is 0.5. If the value of t is equal to one (that is, the A specie or anion reacts with only one proton in Eq. (17)), then Eq. (22) simplifies to the following rate expression:

$$\overrightarrow{r} = \overrightarrow{k}[H^+]^{0.5}. \tag{23}$$

Eq. (23) means that the overall rate of reaction is one-half order in H^+. As mentioned earlier (see Table 1), many dissolution reactions are one-half order in H^+, and the theory developed here presents an uncomplicated explanation for such a fractional order of reaction.

If, on the other hand, the value of t is equal to two, then Eq. (22) becomes:

$$\overrightarrow{r} = \overrightarrow{k}[H^+]. \tag{24}$$

In this case, the overall rate of reaction is first order in H^+. Therefore, the rate of dissolution is expected to be either one-half order or first order in H^+ depending on whether the value of t is one or two. This accounts for the observation that in some solutions the order of reaction is one half, whereas in others it is one. For example, this accounts for the observation mentioned earlier by Majima et al. (1981) that the dissolution of CuO is one-half order with respect to H^+ in sulphuric acid, but first order in perchloric, hydrochloric and nitric acids. In some cases, the anion reacts with one proton, while in other cases it reacts with two protons.

6.3.2. The rate of the reverse reaction and dissolution close to equilibrium
The reverse process, which describes the conditions closer to equilibrium, was first considered by Crundwell and Verbaan (1987). The reverse reactions need to be taken into account in order to derive an expression for the rate of dissolution at equilibrium.

The rate of deposition of cations as M species is given by:

$$r_+ = -k_{c,+}\left[M^{z+}\right] \exp\{-(1-\alpha_+)F\Delta\phi/RT\}. \tag{25}$$

The rate of deposition of the anions is given by:

$$r_- = -k_{c,-}\left[H_t A^{t-a}\right] \exp\{(1-\alpha_-)F\Delta\phi/RT\}. \tag{26}$$

The overall rate of deposition is obtained in a manner similar to described before: (i) set the rates of deposition for both anions and cations equal, (ii) solve for the potential, and (iii) substitute the expression for the potential back into either Eq. (21) or Eq. (26). This algebra yields the following expression for the rate of deposition:

$$\overleftarrow{r} = \left(k_{c,+}\left[M^{z+}\right]\right)^{1-\overline{x}} \left(k_{c,-}\left[H_t A^{t-a}\right]\right)^{\overline{x}} \tag{27}$$

where $\overline{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\}$. This expression may be simplified by lumping parameters together as follows:

$$\overleftarrow{r} = \overleftarrow{k}\left[M^{z+}\right]^{1-\overline{x}}\left[H_t A^{t-a}\right]^{\overline{x}}. \tag{28}$$
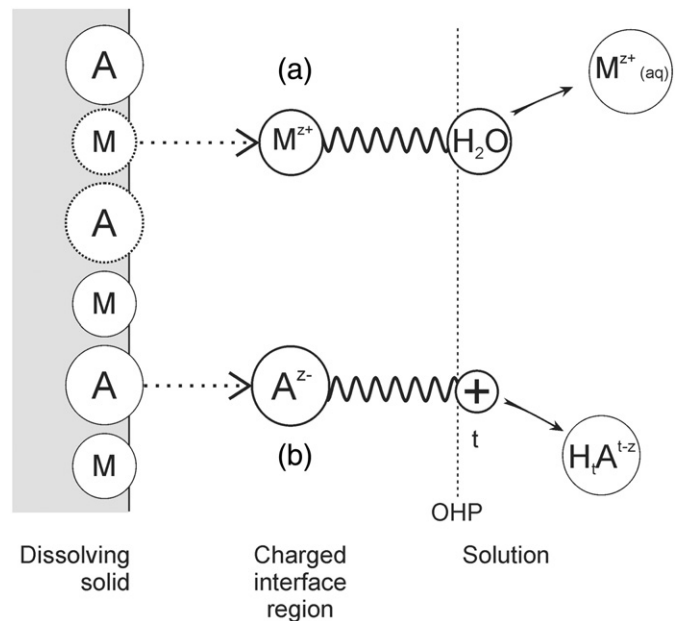

Fig. 5. The dissolution of a solid MA in two separate independent reactions: (a) the removal of M species from the surface by reaction with aqueous species at the OHP to from M^{z+} (aq) cations in solution; (b) the removal of A species from the surface by reaction with t H^+ at the OHP to form $H_t A^{t-z}$ anions in solution.

The values of α_+ and α_- are expected to be close to 0.5. If both α_+ and α_- have values close to one half (or be approximately equal to each other), then the value of $\overleftarrow{x}$ is 0.5. Therefore, the reverse reaction is expected to be one-half order in $[M^{z+}]$ and $[H_tA^{t-a}]$.

6.3.3. The overall rate of dissolution in acidic solutions

The overall rate of dissolution at conditions close to equilibrium is as follows:

$$r = \overrightarrow{k}\left[H^+\right]^{\overrightarrow{x}t} - \overleftarrow{k}\left[M^{z+}\right]^{1-\overline{x}}\left[H_tA^{t-a}\right]^{\overline{x}} \tag{29}$$

where $\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-)$ and $\overline{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\}$.

Crundwell and Verbaan (1987) studied the dissolution of four different samples of sphalerite (ZnS). They reported that their results are consistent with the following expression:

$$r = k_1\left[H^+\right] - k_{-1}\left[Zn^{2+}\right]^{0.43}[H_2S]^{0.56}. \tag{30}$$

Similar experimental results to Eq. (30) were obtained by Romankiw and de Bruyn (1965) and Locker and de Bruyn (1969).

If $\overrightarrow{x}$ and $\overline{x}$ have values for α of one half as discussed earlier, and the value of t is two, Eq. (29) is very close to the experimental results given in Eq. (30). This means that the proposed model is consistent with the experimental results for the entire region of the dissolution reaction, from irreversible dissolution through to reversible dissolution.

6.3.4. Equilibrium conditions

The equilibrium conditions are obtained when the net rate of reaction is zero. The equilibrium condition is given by:

$$K = \frac{\overleftarrow{k}}{\overrightarrow{k}} = \frac{\left[H^+\right]^{\overrightarrow{x}t}}{[M^{z+}]^{1-\overline{x}}\left[H_tA^{t-a}\right]^{\overline{x}}}. \tag{31}$$

The competing models for the description of dissolution, such as the surface-complexation model, the adsorption model, and the precursor model are not able to account for the equilibrium conditions.

Importantly, it should be noted that the rate of dissolution should be determined at conditions that are both far from and close to equilibrium, where possible. If the rate had only been determined far from equilibrium for the example of ZnS given in the previous section, the only feature that requires an explanation is the first order dependence on H^+, which is trivially easy for a large number of kinetic mechanisms. However, the one-half order dependence of the rate of the reverse reaction is not easily explained by any other proposed model. Without this additional information for the reverse reaction, it would be easy to reject the mechanism proposed in this study.

In the next section, the mechanism as outlined above is extended to account for a number of commonly encountered features of dissolution reactions.

### 6.4. Extending the mechanism of dissolution in acidic solutions

The model presented in Section 6.3 will be extended in this section to account for three commonly found features of dissolution: (i) the formation of complexes, (ii) the subsequent reactions that might occur in solution and (iii) the specific adsorption of ions prior to the bond-breaking step.

6.4.1. Effect of complex-forming anions on the rate of dissolution

The removal of metal ions from the surface of the mineral during dissolution may be accompanied by the adsorption of a complex-forming ion. For example, the rate of dissolution of sphalerite is enhanced by the presence of chloride ions. This effect is accounted for by the proposal

that these ions react with surface species or sites that react to form cations (see Fig. 6).

The removal reaction, given by Eq. (15), is modified as follows:

$$\triangleright M_{lat} + cC^{y-} \rightarrow MC_c^{z-cy}(aq) + \triangleright^{z-} \tag{32}$$
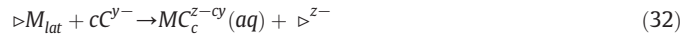
where C^{y-} represents the anion with a charge of $-y$ in the solution (that is, at the outer Helmholtz plane), and c is a stoichiometric coefficient. In this case, the rate of the forward reaction becomes:

$$\begin{aligned}
\overrightarrow{r} &= \left(k_{a,+}[M_{lat}]\left[C^{y-}\right]^c\right)^{1-\overrightarrow{x}}\left(k_{a,-}[A_{lat}]\right)^x\left[H^+\right]^{\overrightarrow{x}t} \\
&= k_1\left[C^{y-}\right]^{(1-\overrightarrow{x})c}\left[H^+\right]^{\overrightarrow{x}t}
\end{aligned} \tag{33}$$

where $\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-)$.

If the value of $\overrightarrow{x}$ is close to 0.5 as discussed before, and the value of c is one, then the order of reaction with respect to C^{y-} is 0.5. If, on the other hand, the value of c is two, then the order of reaction with respect to C^{y-} is 1.

For example, Majima et al. (1980) found that the rate of dissolution of sphalerite, ZnS, was first order in chloride ions. Crundwell and Verbaan (1987) extended their model to account for this effect by assuming that the value of c is two (and the value of $\overrightarrow{x}$ is 0.5) in Eqs. (32) and (33).

6.4.2. Subsequent reactions

The reaction across the Helmholtz layer is the rate-determining step. It does not mean that the products of this reaction are the final products. The rate-determining step may be followed by subsequent steps. One possible subsequent step is further reaction with H^+, as illustrated in Fig. 7. For example, the anion formed by initial dissolution step may react, which would mean that the anion formed during reaction across the solution-solid interface is not the predominant form of the anion in the bulk of the solution (Vetter, 1967).

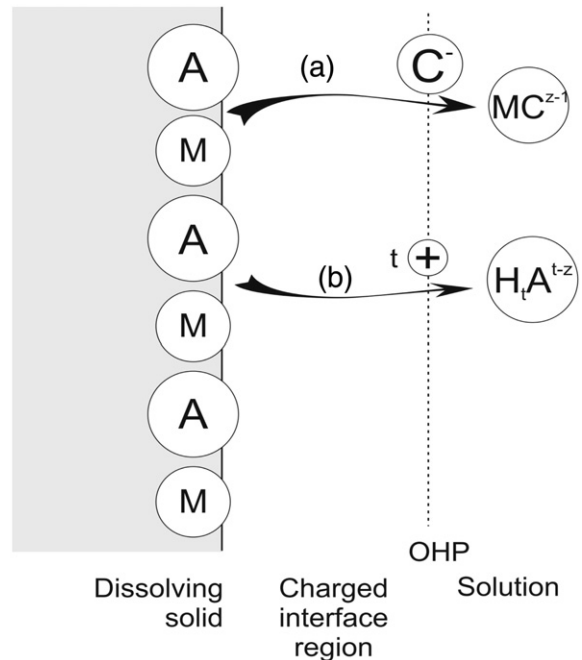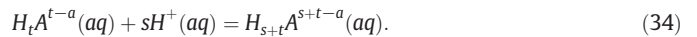For example, the following equilibrium may represent the reactions in the bulk solution:

$$H_tA^{t-a}(aq) + sH^+(aq) = H_{s+t}A^{s+t-a}(aq). \tag{34}$$

Fig. 6. The reaction of the M species at the surface of the solid with complex-forming ions, C^-, at the outer Helmholtz plane.
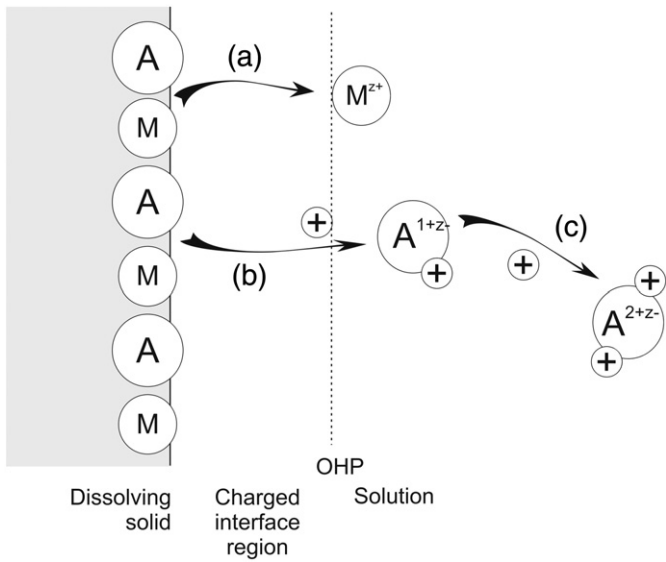
Fig. 7. The reaction of the product of the rate-determining step with other species, in this case H⁺ ions, in the solution to form the final reaction products.

In this case, the rate of removal and deposition of the species that form anions is given as follows:

$$r_- = k_{a,-}[A_{lat}]\left[H^+\right]^t \exp(\alpha_- F\Delta\phi/RT) - k_{c,-}K^{-1}\left[AH_{s+t}^{s+t-a}\right]\left[H^+\right]^{-s} \tag{35}$$
$$\exp\{-(1-\alpha_-)F\Delta\phi/RT\}$$

where K is the equilibrium constant for Eq. (34).

By using the condition that the rate of formation of cations is equal to that for the formation of anions, we are able to derive the following expression for the forward reaction:

$$\overrightarrow{r} = \left(k_{a,+}[M_{lat}]\right)^{1-\overrightarrow{x}}\left(k_{a,-}[A_{lat}]\right)^{\overrightarrow{x}}\left[H^+\right]^{\overrightarrow{x}t} \tag{36}$$

where $\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-)$.

Similarly, the rate of the reverse reaction is by the expression:

$$\overleftarrow{r} = \left(k_{c,+}\left[M^{z+}\right]\right)^{1-\overleftarrow{x}}\left(k_{c,-}K^{-1}\left[H_{s+t}A^{s+t-a}\right]\left[H^+\right]^{-s}\right)^{\overleftarrow{x}} \tag{37}$$

where $\overleftarrow{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\}$.

The values of α_+ and α_- are expected to be close to 0.5, so that the value of x is expected to be close to 0.5. As a result, the reverse reaction is expected to be one-half order in M^{z+} and $H_{s+t}A^{s+t-a}$.

Combining the forward and reverse reactions and collecting constant values, we obtain the following expression:

$$r = \overrightarrow{k}\left[H^+\right]^{\overrightarrow{x}t} - \overleftarrow{k}\left[M^{z+}\right]^{1-\overleftarrow{x}}\left[H_{s+t}A^{s+t-a}\right]^{\overleftarrow{x}}\left[H^+\right]^{-s\overleftarrow{x}}. \tag{38}$$

This expression shows how both the forward and the reverse reactions might be dependent on the pH.

6.4.3. Effect of specific adsorption on the rate of dissolution

In the derivation of the expressions for the rate of dissolution in the previous sections, we have been careful to specify the position of the reacting species with respect to the surface and the outer Helmholtz plane. In all these expressions, the chemical species in the solution that participates in the reaction is at the outer Helmholtz plane, which has the same concentration as the bulk solution. However, there is a possibility that an ion like H⁺ might adsorb at the inner Helmholtz plane (IHP). The inner Helmholtz plane is the distance of closest

approach of these smaller ions. This adsorption itself is dependent on the potential difference across the Helmholtz layer.

In this section, an expression is derived for the adsorption isotherm, and this isotherm is incorporated into an expression for the rate of dissolution. The dissolution mechanism is illustrated in Fig. 8.

Consider the adsorption of H⁺ given by the following expression:

$$\circ + H^+ = \bullet H^+ \tag{39}$$
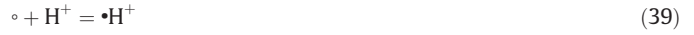
where ∘ represents an available or unoccupied site similar to our previous notation A_{lat}, and • H⁺ represents an occupied site on the surface at the inner Helmholtz plane (which could also have been represented as HA_{lat}).

The proportion of the total surface that is occupied by • H⁺ is given by θ. The rate of the adsorption and desorption from the surface is given by:

$$r_{ads} = k_{ads}\left[H^+\right](1-\theta)\exp(\alpha_{ads}F\Delta\phi/RT) - k_{-ads}\theta\exp(-(1-\alpha_{ads})F\Delta\phi/RT). \tag{40}$$

If it is assumed that the adsorption and desorption of H⁺ are faster than dissolution, then this rate is close to zero, and an expression for θ can be derived:

$$\theta = \frac{k_{ads}\left[H^+\right]}{k_{-ads}\exp(F\Delta\phi/RT) + k_{ads}[H^+]}. \tag{41}$$

The development of Eq. (41) parallels that of Eq. (7). The difference is the incorporation of the effect of the potential difference at the surface.

If the rate of dissolution is dependent on the coverage of surface by the adsorbed proton, and the whole HA_{lat}^{1-a} species moves from the surface to the outer Helmholtz plane, then the rate expression for the forward reaction is given as follows:

$$r_- = k_{-,a}\theta\exp(-\alpha_\bullet F\Delta\phi/RT) \tag{42}$$

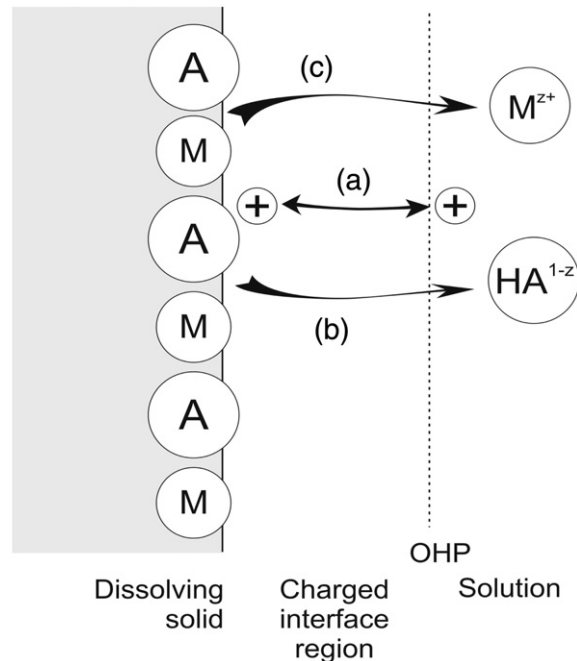where $\alpha_\bullet$ is the charge transfer coefficient for the transferring HA^{1-a} species.

Fig. 8. The specific adsorption of an H⁺ ion at the inner Helmholtz plane.

A simplified expression will be derived now by assuming that the coverage of the surface is low. Under these conditions, the surface coverage is given as follows:

$$\theta = \frac{k_{ads}[\mathrm{H}^+]}{k_{-ads}\exp(F\Delta\phi/RT)}.$$ (43)

Eq. (43) represents a potential-dependent isotherm at low surface coverage.

The combination of Eqs. (42) and (43) gives the following expression for the rate of removal of anions from the surface:

$$r_- = k_{-,a}\frac{k_{ads}}{k_{-ads}}\left[\mathrm{H}^+\right]\exp\{-\alpha_\bullet-1)F\Delta\phi/RT\}.$$ (44)

The following expression for the rate of dissolution is obtained by combining Eq. (42) with the expression for the rate of removal of cations, Eq. (16). This yields the following rate equation:

$$\vec{r} = \vec{k}\left[\mathrm{H}^+\right]^{\vec{x}t}$$ (45)

where $\vec{x} = \alpha_+/(\alpha_+ + \alpha_\bullet + 1)$.

This rate expression has a slightly different order of reaction than before. For example, if the values of the transfer coefficients are all equal to one half, then the value of $\vec{x}$ is 0.25.

Specific adsorption might account for some of the variation in the measured order of reaction that has been reported.

6.5. Derivation of the rate of dissolution in alkaline solutions

A rate expression for the dissolution of minerals in alkaline solutions is developed in this section.

6.5.1. Rate of dissolution far from equilibrium

The proposed mechanism of dissolution is shown in Fig. 9. In acidic solutions, H$^+$ ions form complexes with the sites on the surface that result in anions on dissolution. In contrast, in alkaline solutions OH$^-$ ions interact with the sites on the surface that result in cations to form

Fig. 9. The proposed mechanism of dissolution in alkaline solution: (a) the bonds of M species with the surface break and at the same time bonds begin to form with hydroxide ions, eventually forming M^{z+} ions that are complexed with hydroxide ions; (b) the bonds of A species break and bonds with the solvent form, resulting in the formation of A^{z-} (aq) ions.

complexes. Consequently, the bond-breaking and cation transfer reaction is given as follows:

$$\triangleright M_{lat} + r\mathrm{OH}^- \rightarrow M(\mathrm{OH})^{z-r}_{rt}(aq) + \triangleright^{z-}$$ (46)
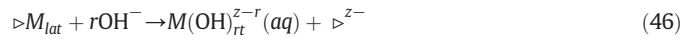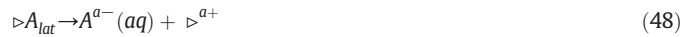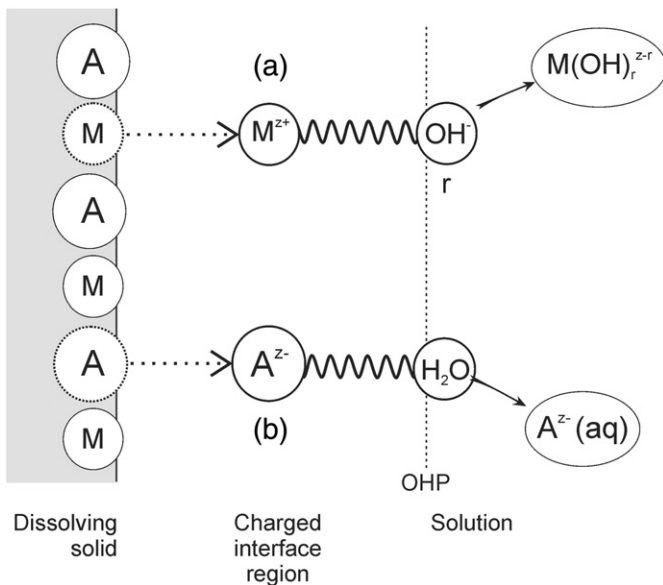
where r is the stoichiometric number of OH$^-$ ions reacting with the metal site, and, as before, $\triangleright^{z-}$ represents the uptake of excess charge by the surface. This uptake could be in the form of an electron or a hole.

The rate of formation of cations from the surface is given by:

$$r_+ = k_{a,+}[M_{lat}][\mathrm{OH}^-]^r\exp(\alpha_+ F\Delta\phi/RT).$$ (47)

The formation of anions from the surface is given as:

$$\triangleright A_{lat} \rightarrow A^{a-}(aq) + \triangleright^{a+}$$ (48)

and the rate of formation of these anions from the surface is given by:

$$r_- = k_{a,-}[A_{lat}]\exp\{-\alpha_- F\Delta\phi/RT\}.$$ (49)

Since the dissolution is congruent and stoichiometric, rate of formation of cations is equal to the rate of formation of anions, Eqs. (47) and (49) can be combined to give the following expression for the potential of the dissolving surface:

$$\Delta\phi = \frac{RT}{F(\alpha_+ + \alpha_-)}\ln\left(\frac{k_{a,-}[A_{lat}]}{k_{a,+}[M_{lat}][\mathrm{OH}^-]^r}\right).$$ (50)

Substitution of Eq. (50) back into Eq. (47) yields an expression for the rate of the forward reaction, $\vec{r}$:

$$\vec{r} = \left(k_{a,+}[M_{lat}][\mathrm{OH}^-]^r\right)^{1-\vec{x}}\left(k_{a,-}[A_{lat}]\right)^{\vec{x}} = \vec{k}[\mathrm{OH}^-]^{r(1-\vec{x})}$$ (51)

where $\vec{x} = \alpha_+/(\alpha_+ + \alpha_-)$.

The order of reaction is one-half if the value of r is one, and one if the value of r is two.

The kinetics of dissolution of several of the silicate minerals has orders of reaction with respect to OH$^-$ that are fractional. For example, the rate of dissolution of quartz, SiO$_2$, in alkaline solutions has an order of reaction with respect to OH$^-$ that is close to 0.5 (Brady and House, 1996), which is close to the values predicted here.

6.5.2. Rate of the reverse reaction and dissolution closer to equilibrium

For the reverse reaction to the removal of anions is the deposition of cations. The rate of deposition is given by:

$$r_+ = -k_{c,+}[M(\mathrm{OH})^{z-r}_r]\exp\{-(1-\alpha_+)F\Delta\phi/RT\}.$$ (52)

The rate of deposition of the anions is given by:

$$r_- = -k_{c,-}[A^{a-}]\exp\{(1-\alpha_-)F\Delta\phi/RT\}.$$ (53)

The overall rate of deposition is obtained in a manner similar to described before. This yields the following expression for the rate of deposition of cations and anions:

$$\overleftarrow{r} = \left(k_{c,+}[M(\mathrm{OH})^{z-r}_r]\right)^{1-\overleftarrow{x}}\left(k_{c,-}[A^{a-}]\right)^{\overleftarrow{x}}$$ (54)

where $\overleftarrow{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\}$. This expression may be simplified by lumping parameters together as follows:

$$\overleftarrow{r} = \overleftarrow{k}[M(\mathrm{OH})^{z-r}_r]^{1-\overleftarrow{x}}[A^{a-}]^{\overleftarrow{x}}.$$ (55)

The values of α_+ and α_- are expected to be close to 0.5. Therefore, the reverse reaction is expected to be one-half order in $[M(OH)_r^{z-r}]$ and $[A^{a-}]$.

6.5.3. Overall rate of dissolution in alkaline solutions

The overall rate of dissolution at conditions close to equilibrium is as follows:

$$r = \overrightarrow{k}\,[OH^-]^{r(1-\overrightarrow{x})} - \overleftarrow{k}\,[M(OH)_r^{z-r}]^{1-\overline{x}}\,[A^{a-}]^{\overline{x}} \tag{56}$$

where $\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_- z_-)$ and $\overline{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\}$.

6.5.4. Equilibrium conditions

The equilibrium conditions are obtained when the net rate of reaction is zero:

$$K = \frac{\overleftarrow{k}}{\overrightarrow{k}} = \frac{[OH^-]^{r(1-\overrightarrow{x})}}{[M(OH)_r^{z-r}]^{1-\overline{x}}\,[A^{a-}]^{\overline{x}}} \tag{57}$$

where $\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-)$ and $\overline{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\}$.

Thus, the mechanism of dissolution is able to describe the dissolution of minerals both far from and close to equilibrium, and in acidic and alkaline conditions. This mechanism will be applied to various systems in a subsequent paper.

7. Discussion

The rate expression for the proposed mechanism of dissolution for various scenarios is given in Table 2 (under conditions in which diffusional influences are absent). These rate expressions admit the following possible orders of reaction: 0.25, 0.5, 1.0, and 1.5. As discussed in Section 3, the experimental results are centred on values of 0.5, 1 or 1.5, in agreement with the simplest of the scenarios analysed in this paper.

The reverse reactions are also important. They have been investigated particularly for the sulphides. The rate expressions for the reverse reaction are given in Table 3. The proposed mechanism of dissolution for

the reverse reaction gives orders of reaction that are half order for all cases. This is a good test of the mechanism proposed here, and as mentioned earlier, this result is in agreement with the experimental results for the non-oxidative dissolution of several sulphides (Crundwell and Verbaan, 1987; Locker and de Bruyn, 1969).

8. Conclusions

The key parameter for the interpretation of kinetic mechanisms is the order of reaction. Experimentally, it is found that the order of reaction has values that are close to one half. The models currently in use, such as the surface-complexation model and the adsorption model, are not able to provide a derivation of the rate expression that has half-order kinetics. As a result, these models fail to describe the primary phenomenon occurring at the mineral surface during dissolution.

A model that is based on the breaking of the bond at the surface and the kinetics of transfer of the resulting ions across the solid–solution interface has been developed in this work. This model is able to describe the observed orders of reaction, which are either one half or one with respect to H^+ or OH^-. For specific adsorption, an order of reaction of 0.25 is predicted.

The proposed model was used to derive expressions for the rate of reaction for a wide variety of dissolution phenomena and conditions. These models are in general agreement with the experimental data.

Appendix A

In general, the rate constant, k, for the removal of a species, M_{lat}, from the surface of a mineral by reaction with water (see Eq. (15)) is given by:

$$k = \frac{k_B T}{h}\exp\left(-\frac{\Delta\overline{G}^\#}{RT}\right) \tag{A1}$$

where k_B is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, R is the gas constant and $\Delta\overline{G}^\#$ is the Gibbs free energy of activation.

Table 2
Summary of derived rate expressions for the forward reaction.

Reactions with protons	x	t	c	Order of reaction wrt H^+	Rate expression
The variable t refers to the number of H^+ ions that react with the A_{lat} sites of the surface in the rate-determining step.					
The variable c refers to the number of C^{y-} ions that react with the M_{lat} sites of the surface in the rate-determining step.					
$MA + tH^+ \rightarrow M^{z+} + H_t A^{t-a}$	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-) = 0.5$	1		0.5	$\overrightarrow{r} = \overrightarrow{k}\,[H^+]^{0.5}$
	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-) = 0.5$	2		1	$\overrightarrow{r} = \overrightarrow{k}\,[H^+]$
	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-) = 0.5$	3		1.5	$\overrightarrow{r} = \overrightarrow{k}\,[H^+]^{1.5}$
$MA + tH^+ + cC^{y-} \rightarrow MC_c^{z-cy}(aq) + H_t A^{t-a}$	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-) = 0.5$	1	1	0.5	$\overrightarrow{r} = \overrightarrow{k}\,[C^-]^{0.5}[H^+]^{0.5}$
	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-) = 0.5$	2	1	1	$\overrightarrow{r} = \overrightarrow{k}\,[C^-]^{0.5}[H^+]$
$MA + tH^+ \rightarrow M^{z+} + H_t A^{t-a}$ with specific adsorption	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_- + 1) = 0.25$	1		0.25	$\overrightarrow{r} = \overrightarrow{k}\,[H^+]^{0.25}$
	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_- + 1) = 0.25$	2		0.5	$\overrightarrow{r} = \overrightarrow{k}\,[H^+]^{0.5}$

Reactions with hydroxide ions	x	r	c	Order of reaction wrt to OH^-	Rate expression
The variable r refers to the number of OH^- ions that react with the A_{lat} sites of the surface in the rate-determining step.					
The variable c refers to the number of C^{y-} ions that react with the M_{lat} sites of the surface in the rate-determining step.					
$MA + rOH^- \rightarrow M(OH)_r^{z-r} + A^{a-}$	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-) = 0.5$	1		0.5	$\overrightarrow{r} = \overrightarrow{k}\,[OH^-]^{0.5}$
	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-) = 0.5$	2		1	$\overrightarrow{r} = \overrightarrow{k}\,[OH^-]$
$MA + rOH^- \rightarrow M(OH)_r^{z-r} + A^{a-}$	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-) = 0.5$	1		0.5	$\overrightarrow{r} = \overrightarrow{k}\,[OH^-]^{0.5}$
	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_-) = 0.5$	2		1	$\overrightarrow{r} = \overrightarrow{k}\,[OH^-]$
$MA + rOH^- \rightarrow M(OH)_r^{z-r} + A^{a-}$	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_- + 1) = 0.25$	1		0.25	$\overrightarrow{r} = \overrightarrow{k}\,[OH^-]^{0.25}$
With specific adsorption	$\overrightarrow{x} = \alpha_+/(\alpha_+ + \alpha_- + 1) = 0.25$	2		0.5	$\overrightarrow{r} = \overrightarrow{k}\,[OH^-]^{0.5}$

Table 3
Summary of the derived rate expressions for the reverse reaction.

Reaction	x	t	Order of reaction	Rate expression
The variable t refers to the number of H^+ ions that react with the A_{lat} sites of the surface in the rate-determining step.				
$M^{z+} + H_tA^{t-a} \rightarrow MA + tH^+$	$\bar{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\} = 0.5$	1	0.5	$\overleftarrow{r} = \overleftarrow{k}\,[M^{z+}]^{0.5}\,[HA^{1-a}]^{0.5}$
	$\bar{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\} = 0.5$	2	0.5	$\overleftarrow{r} = \overleftarrow{k}\,[M^{z+}]^{0.5}\,[H_2A^{2-a}]^{0.5}$

Reaction	x	r	Order of reaction	Rate expression
The variable r refers to the number of OH^- ions that react with the A_{lat} sites of the surface in the rate-determining step.				
$M(OH)_r^{z-r} + A^{a-} \rightarrow MA + rOH^-$	$\bar{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\} = 0.5$	1	0.5	$\overleftarrow{r} = \overleftarrow{k}\,[M(OH)^{z-1}]^{0.5}\,[A^{a-}]^{0.5}$
	$\bar{x} = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\} = 0.5$	2	0.5	$\overleftarrow{r} = \overleftarrow{k}\,[M(OH)_2^{z-2}]^{0.5}\,[A^{a-}]^{0.5}$

The rate of removal of a species from the surface of a solid to solution involves the breaking of the bond with the surface, and the formation of a solvation sheath around the ion, all under the influence of the potential difference across the Helmholtz plane. Electrochemical electron transfer and homogeneous electron transfer, although not exactly the same as that considered here, have been studied in detail (Marcus, 1956; Gerischer, 1960; Morrison, 1980; Miller et al., 1995). The rates of these reactions have been shown to be determined by the reorganization of the solvent sheath (Marcus, 1956). Ion transfer reactions have not received nearly as much attention. However, solvent effects play a major role in determining the rate of reaction (Schmickler, 1995). It is reasonable, therefore, to propose that the rate of removal of a species from a position on the surface to the outer Helmholtz plane is strongly influenced by the formation of the solvation sheath. The activation energy for the removal of the M species from the surface and the formation of the solvation sheath can be approximated by the reorganization energy of the solvation sheath described by the fluctuating energy model (Morrison, 1980). This is given as follows:

$$\Delta\overline{G}^{\#} = \frac{\left(\lambda + \Delta G^0 - F\Delta\phi\right)^2}{4\lambda} \qquad (A2)$$

where ΔG^0 is the standard Gibbs free energy of the reaction, λ is the reorganization energy, F is Faraday's constant, $\Delta\phi$ in the change in potential difference across the Helmholtz plane. The conditions that ΔG^0 is much less than 2λ, and that $\Delta\phi$ is less than $4\lambda/F$ are frequently met for reactions in aqueous solutions (Levich, 1970; Morrison, 1980). Using these conditions, Eq. (A2) can be written as follows:

$$\Delta\overline{G}^{\#} = \frac{\left(\lambda + \Delta G^0\right)^2}{4\lambda} - \frac{F\Delta\phi}{2}. \qquad (A3)$$

The substitution of Eq. (A3) into Eq. (A1) yields:

$$k = k_f \exp\left(\frac{\Delta\phi F}{2RT}\right) \qquad (A4)$$

where k_f is a collection of constants. The rate of Eq. (15), for example, is given by:

$$rate = k[M_{lat}][H_2O]^w. \qquad (A5)$$

The substitution of Eq. (A4) into Eq. (A5), yields:

$$rate = k[M_{lat}][H_2O]^w \exp\left(\frac{\Delta\phi F}{2RT}\right). \qquad (A6)$$

Inspection of Eq. (A6) and Eq. (16) reveals that the value of α_+ is expected to be close to one-half. The proposal that the rate of reaction is determined by the solvation of the surface ion under the influence of the potential difference across the surface is supported, in part, by the observation that the rate of reaction of metal oxides and silicates is strongly correlated with the water exchange rate in the inner sphere of the corresponding metal ion. This correlation for metal oxides is shown in Fig. A1.

Appendix B

The model proposed by Vermilyea (1966) has been criticised from two points of view that might be transferred to the mechanism proposed in this paper. These criticisms are addressed here.

(i) Blesa et al. (1994) rejected Vermilyea's work based on the argument that the work done to move ion across the double layer would typically require below 30 kJ/mol. This value does not agree with the experimental values for the activation energy, which are typically in the range of 40–80 kJ/mol.
However, Blesa's calculation ignores the displacement, rearrangement and polarisation of water molecules during ion-transfer. This is a critical omission. Marcus (1956) showed that the rearrangement of the water molecules is the rate-controlling step even for simple homogeneous electron-transfer reactions. Schmickler (1995) indicated that water rearrangement might be the rate-controlling step in ion-transfer reactions. The re-organisation of the water molecules has an activation energy of between 0.5 and 1.0 eV, that is, 48–96 kJ/mol (Miller et al., 1995), which is in the range reported for dissolution reactions. The mechanism proposed here is based on bond-breaking and ion-formation, it is expected the water rearrangement is the rate-controlling step. This
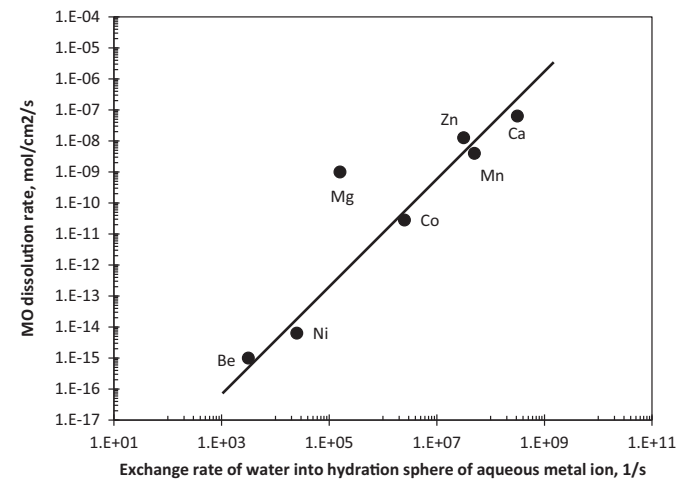
Fig. A1. The correlation between the rate of dissolution and the exchange rate of water in the inner solvation sheath of the ion. This correlation supports the proposal that the rate limiting step in the development of Eq. (A6) and Eq. (16) is the formation and arrangement of the solvation sheath around the ion during departure from the surface.

discussion shows that the reasoning of Blesa et al. (1994) cannot be defended.

(ii) Olsen (2007) rejected Vermilyea's work based on an argument that models based on potential should be dependent on ionic strength, and that measured rates of dissolution do not depend on ionic strength. As discussed in Section 6, the potential difference is composed of two layers: (i) the Helmholtz layer, which is a narrow, rigid layer with a linear potential profile close to the surface; and, (ii) the Gouy layer, which is a thicker, more diffuse layer. The potential difference across the Helmholtz layer is not dependent on ionic strength, whereas that of the Gouy layer is. Vermilyea (1966) and particularly Diggle (1973) make it clear that the potential difference that they refer to is that across the Helmholtz plane. The reasoning of Olsen (2007) cannot be defended.

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